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STRUCTURAL–PHASE CHANGES OF NATURAL CRYSTALLINE QUARTZ DURING FLUORIDE PROCESSING

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New information is obtained on the structural changes occurring during fluoridizing of natural crystalline quartz by ammonium hydrogen fluoride. The morphological, structural, and phase particulars of the samples at each stage of fluoride processing of natural crystalline quartz are studied. Scanning electron microscopy is used to study the morphology, microstructure, and particle-size distribution. X-ray phase analysis and IR spectroscopy are used to determine the phase composition of the samples.

Key words: silica-containing raw material, ammonium hydrogen fluoride, ammonium hexafluorosilicate, amorphous silica.

Interest in areas of science and engineering which are based on the use of different forms of silica — a unique material used for various purposes — has been increasing rapidly in the last few decades. The following have found diverse applications: selective silica adsorbents and absorbers; carriers of the active phase in catalysts; fillers including reinforcing fibers for polymer systems; thickeners of disperse media; binders for molding materials; carriers for gas chromatography; and, others. Chemical surface modification of disperse amorphous silica, which makes it possible to change purposefully the adsorption properties and technological characteristics of synthesized composite materials, has undergone enormous advancement.

RESEARCH APPARATUS AND METHODS

The principal methods of observation for studying structure and internal microstructure and determining the microparticle size of samples of natural crystalline quartz and amorphous silica was scanning electron microscopy. The investigations were performed with a LEO-1420 scanning electron microscope (voltage 20 kV) whose magnification range is $\times 12 - 257,000$. The analytical work was performed at the Analytical Center for Mineral – Geochemical Research

at the Institute of Geology and Use of the Environment of the Far-East Branch of the Russian Academy of Sciences (analyst T. B. Makeeva). The information content of the data obtained with the LEO-1420 high-resolution scanning electron microscope is based on the interaction of an electron beam with the experimental object. The surface of the object is irradiated with a finely focused electron beam, which can either be at rest or swept in a raster along the surface of the sample. In so doing, the method of obtaining an image in secondary electrons (SEI) is used. The ultrafine structure (transmission electron microscopy — TEM) of a nanodisperse amorphous silicon sample was studied with a JEOL 2200 FS scanning microscope (voltage 200 kV, field emission regime (FEG), and a columnar energy filter) was studied at the Institute of Solid-State Chemistry at the National Center for Scientific Research in Bordeaux, France (analyst G. Magamel).

X-ray phase analysis was used to identify different phases. The identification was made by analyzing the diffraction pattern engendered by samples of quartz sand, ammonium hexafluorosilicate, and amorphous silica using the Debye – Scherrer method. The following were used: a DRON-3M diffractometer with CuK_α radiation (tube voltage 30 kV, current 25 mA, slits 2, 4, and 0.25, Ni filter, goniometer velocity $1^\circ/\text{min}$, diaphragm ribbon velocity 720 mm/h) and a D8 Advanced Diffractometer (Bruker Company; CuK_α radiation, Ni filter, current 20 mA, tube voltage 40 kV, scan rate $300^\circ/\text{min}$, reproducibility ± 0.00010). All samples were photographed under identical measurement conditions. The phases were identified using XRD data for mineral identifi-

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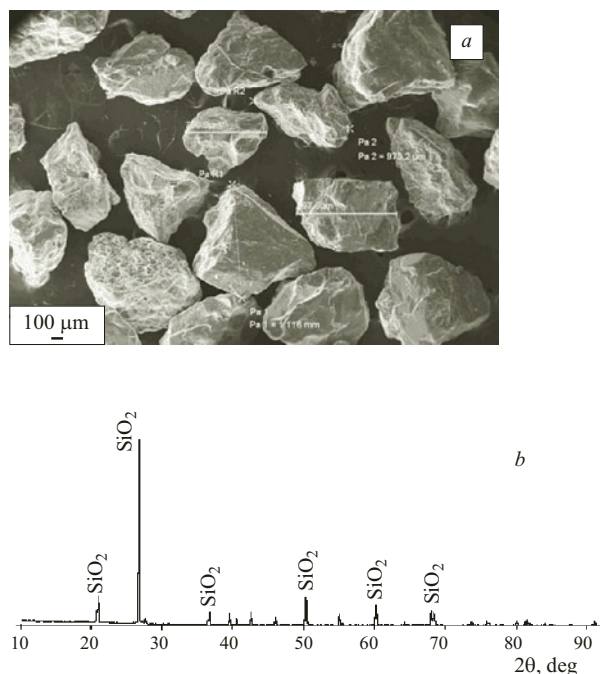


Fig. 1. Quartz sand from Primor'e: *a*) photomicrograph; *b*) x-ray diffraction pattern.

cation, compiled by V. I. Mikheev and E. P. Saldaу [1, 2], and the JCPDS international standard XRD data card file.

The samples obtained were identified by IR spectroscopy performed with a Perkin Elmer IR-Fourier Spectrum One Spectrometer 2002. The measurements were performed in the range $4000 - 400 \text{ cm}^{-1}$ with resolution 4 cm^{-1} and 16 scans/min.

EXPERIMENTAL PART

Quartz sands containing up to 95%⁴ silicon dioxide obtained from the quartz-containing mineral material from the Chalgan field in Amur Oblast. The content of the principal impurities Al, Fe, Ti, Ca, Na, Mg, and Mn is $10^{-3} - 10^{-4}\%$ with the content of other impurities, including Pb, Cu, Cr, V, Ba, Zr, and Sr, not exceeding $10^{-4}\%$. No other elements were found.

The results of particle-size analysis of quartz sand from the Chalgan field in Primor'e show that the principal grain sizes range from 0.2 to 1 mm, whose fraction is 63.4%. The quartz content is 99% in the particle-size fraction $> 1.0 \text{ mm}$ (yield in the total amount 16.92%), 75% in the size fraction $< 0.15 \text{ mm}$ (5.13%), and 95% in the main fraction with particle size from 0.15 to 1.0 mm (77.95%).

A study of the morphological characteristics of quartz molding sands from the Chalgan field in Amur Oblast showed that the particle size fluctuates from 0.8 to 2.7 mm and the particles have a uniform surface (Fig. 1*a*).

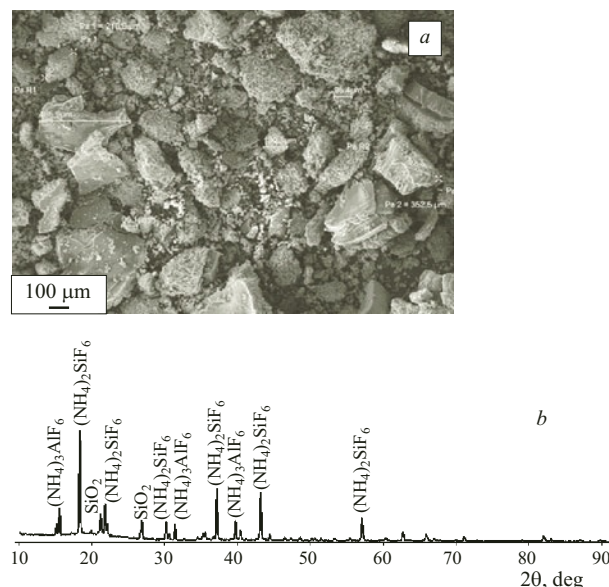


Fig. 2. Product obtained at the interaction stage at temperature 200°C : *a*) photomicrograph; *b*) x-ray diffraction pattern.

In different chemical processes which one or another structure undergoes the transition from one stage to another is always accompanied by a large change in the morphology of the sample. The morphology of the quartz-sand particles is characterized by crystalline faceting as well as smooth shapes; the sand particles are smooth. Traces of deformation and distinct shear surfaces along the shear planes are often observed on the surfaces of particles with crystalline faceting. Idiomorphic crystals with rounded corners are characterized by a small relief and furrow-like structures with traces of leaching. When the microstructure of such particles is studied under high magnification ($\times 500 - 3000$) a layered porous structure is often observed sporadically. The appearance of such a furrow-layered structure of the crystal surface can be explained by selective dissolution of sections with weakened interatomic bonds on the surface of the faces [3]. Aside from the principal morphological shapes described above, individuals whose morphology is characterized by smoothed compact shapes are also encountered. Most particles of the initial silica have a deformed structure due to mechanical damage (stresses) as well as natural corrosive media on a surface.

X-ray phase analysis of the initial quartz sand performed in a laboratory by physical methods at the Institute of Materials Science of the Far-East Branch of the Russian Academy of Sciences (Khabarovsk) showed that the quartz consists of a polymorphic modification of $\beta\text{-SiO}_2$, which is stable at normal temperature and pressure (Fig. 1*b*).

Figure 2*a* shows the morphological character of the product obtained. After the initial quartz sand is treated with ammonium hydrogen fluoride the surfaces of its large crystals, reaching 2 – 3 mm in size, acquire smaller crystals ranging in size from 1 to 10 μm and crystal microparticles from

⁴ Here and below, content by weight.

250 to 500 nm. The micromorphology of the small, partially or even completely rounded, crystals is close to oval and spherical shapes with fusion microstructures. Some large individual crystals of the initial silicon dioxide with traces of damage have a microglobular base with characteristic globule sizes from 100 to 250 nm.

The microstructure of the layers is also microglobular but with globules ranging in size from 400 to 550 nm, which is larger than the microglobules in the base. The microglobules of the separated layers undergo sintering, forming a porous structure. Aside from the porous structures on the surface of the base with a microglobular structure, sections with a smoother, dense structure, probably formed as a result of sintering of microglobules smaller than 100 nm, are also observed sporadically. It can be supposed that the small crystals of the initial silicon dioxide, sticking to the large crystals, are formed as a result of the destruction of the large initial silicon dioxide crystals due to the action of the corrosive medium — ammonium hydrogen fluoride NH_4HF_2 . The numerous cracks and microcracks on the surface of large crystals also attest to an interaction of the initial silicon dioxide material with NH_4HF_2 .

The product obtained at 200°C with soaking time 3 h is a white powder. X-ray phase analysis revealed the presence of the phases $(\text{NH}_4)_2\text{SiF}_6$, SiO_2 and $(\text{NH}_4)_3\text{AlF}_6$ (Fig. 2b).

The product obtained was purified to ammonium hexafluoride by sublimation at temperatures to 400°C on a setup with special structure. $(\text{NH}_4)_2\text{SiF}_6$ sublimates quickly; the degree of formation of this product is > 98% [4].

The formation of volatile ammonium hexafluoride $(\text{NH}_4)_2\text{SiF}_6$ leads to the formation on the surface of the desublimator of structures assembled from thin nanosize microplates with thickness ≥ 200 nm (Fig. 3a). Examination of the microstructure of the silica powder at this stage shows that the microplates stick to one another forming, together with fibrous structures, apical pyramidal and dendritic forms.

The ammonium hexafluorosilicate obtained as a result of sublimation is of high purity. This is confirmed by data from emission spectral and x-ray phase analysis. The content of the impurities (Al, Fe, Mn, Mg, Cu) does not exceed $10^{-3} - 10^{-5}\%$. This is because during sublimation the impurity compounds of Al, Fe, Na, and K form simple fluorides, which remain in the nonvolatile residue [5]. Figure 3b displays an x-ray diffraction pattern of the ammonium hexafluorosilicate obtained and the distribution of the phases in the sample. The product is largely represented by principal phase $(\text{NH}_4)_2\text{SiF}_6$. The distribution of the phases in this sample is as follows: $(\text{NH}_4)_2\text{SiF}_6$ — 97%; SiO_2 — 3%; the computed fluorine content — 55.85%; the fluorine content from chemical analysis — 56.33% (the analysis was performed at the Analytical Center of the All-Russia Scientific–Research Institute of Chemical Technology, JSC), which agrees well with the computed content.

According to [6] ammonium hexafluorosilicate is stable to 100°C. Above this temperature it starts to lose mass (about

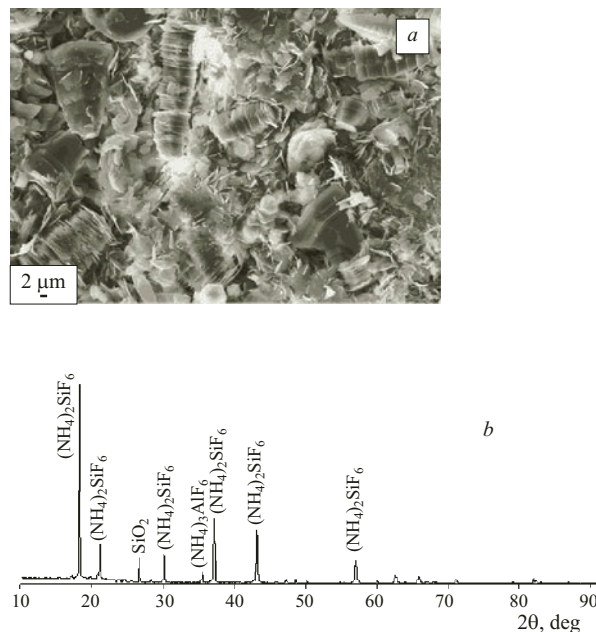


Fig. 3. Ammonium hexafluorosilicate obtained at temperature 350°C: a) photomicrograph; b) x-ray diffraction pattern.

0.2%/h) and at higher temperatures it sublimates with no change in the composition. The ammonium hexafluorosilicate phase and its purity were studied at the Institute of Chemistry of the Far-East Branch of the Russian Academy of Sciences (Vladivostok) [7]. The ammonium hexafluorosilicate obtained from quartz sands is re-sublimated in a furnace and the sublimate and residue compositions were studied. Silicon dioxide was also found in the ammonium hexafluorosilicate obtained. In the opinion of the authors, the presence of SiO_2 in the desublimite can be explained by “trapping” of microparticles of the trace impurity SiO_2 by the very rapidly sublimating $(\text{NH}_4)_2\text{SiF}_6$. The contamination of the desublimite by silicon dioxide can be avoided by keeping the sublimation temperature low and at the same time reaching a low degree of sublimation [8–9]. However, the technology can be unprofitable under such conditions.

Amorphous silica was obtained by hydrolysis of ammonium hexafluorosilicate by an ammonia solution in a water-alkali solution via the reaction



The silica obtained is a nanodisperse powder [10] with primary nanoparticles not exceeding 20 nm in diameter (Fig. 4a). The structure of the silica has changed to amorphous (Fig. 4b).

Figure 5 displays the IR spectra of the initial material and amorphous silica. The character of the peaks has changed and the lines of the quartz sand sample are lower than the amorphous silica lines, indicating something about the character of the structural transformations and a change in the dispersity of the samples. Bands due to the presence of water of crystallization are present in all IR spectra. The ab-

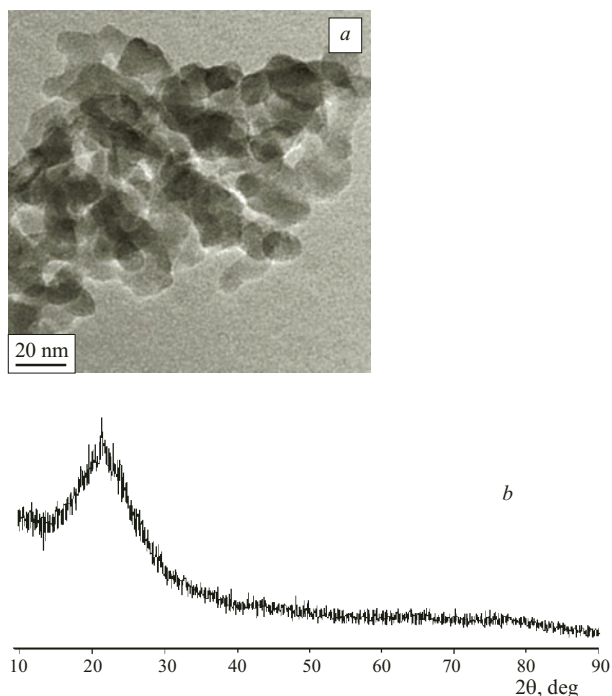


Fig. 4. Amorphous silica obtained by fluoride technology: *a*) photomicrograph; *b*) x-ray diffraction pattern.

sorption bands due to the stretching vibrations of H_2O molecules ($\nu = 3200 - 3550 \text{ cm}^{-1}$) and deformation vibrations of H_2O ($\nu = 1600 - 1630 \text{ cm}^{-1}$) are clearly visible in the spectra. The band at 3680 cm^{-1} is due to O–H vibrations of hydroxyl groups occupying contact sites, which are almost inaccessible for large molecules, of the particles or located in pores of molecular size.

CONCLUSIONS

It can be concluded on the basis of the material presented above that the dispersity changes and the crystal structure of the initial natural quartz becomes amorphous during fluoride processing. The amorphous silica obtained by this method is characterized by the smallness of the particles which are in a stable thermodynamic state. Such silicon with amorphous structure is highly hydrophobic.

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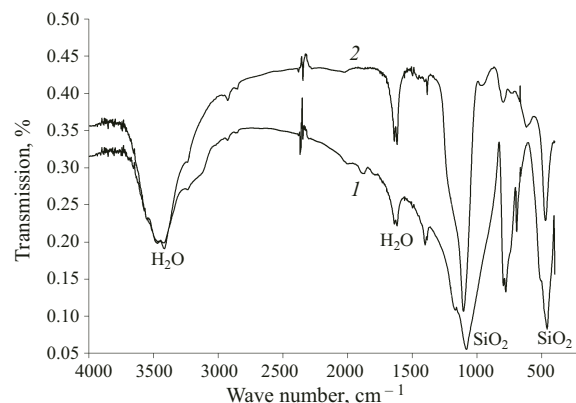


Fig. 5. IR spectra of samples of the initial quartz sand (*1*) and the amorphous silica (*2*) obtained from it.

ing, low-waste, and environmentally safe technologies for complex processing of the natural resources of Primor'e" (government registration number 01.2.00606189).

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